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**CHEMICAL DYNAMICS STUDIES OF UNIMOLECULAR REACTIONS
IN ENERGETIC MATERIALS**

FINAL TECHNICAL REPORT

(Report Period: August 1, 1992 - July 31, 1996)

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Abstract

Research performed over the period August 1, 1992 to July 31, 1996 supported by the U.S. Army Research Office (Grant number: DAAL03-92-G-0358) is described. This research project was concerned with the development of methods and simulations to study the unimolecular reaction dynamics of polyatomic molecules of interest as energetic materials. The research consisted of classical dynamics studies of the fundamental dynamics, mode selectivity, IVR in highly excited polyatomic molecules, and simulations of unimolecular reactions. Much of the effort was devoted to developing an improved potential energy surface to describe the unimolecular dissociation of RDX (hexahydro-1,3,5-trinitro-s-triazine).

RESEARCH

Our research during the grant period consisted of studies of the fundamental dynamics, mode selectivity, IVR in highly excited polyatomic molecules, and simulations of unimolecular reactions.

We are interested in understanding the elementary chemical reactions of energetic materials, particularly how they behave under various conditions. We have focused mainly on unimolecular reactions of RDX, and thus we have studied the rates and pathways by which energy is redistributed in the molecule. Previously, we performed extensive studies of intramolecular vibrational energy redistribution (IVR) in a wide range of molecules. Perhaps the most important result of those studies is that when a particular mode or combination of modes of a molecule are highly excited the excitation energy flows out to the other molecular modes along well-defined pathways. Yet, as many theoretical and experimental studies have shown, there is sufficiently rapid "randomization" of the excitation energy such that mode selective reaction is usually not observed. This has often been interpreted to mean that the dynamics of the reacting molecules are chaotic or ergodic, perhaps, in part, because studies have shown that the dynamics of triatomic molecules can be chaotic at energies well below dissociation thresholds. This coupled with the general observations of statistical behavior of reactions was often extrapolated to the general conclusion that all (or most) molecules, regardless of size, are undergoing chaotic motion when they react.

This situation prompted us to carry out calculations to explore the fundamental nature of the dynamics of molecules above their reaction thresholds. For example, in an earlier study, we computed power spectra for a variety of molecules (C_2H_4 , CH_3ONO , and SiF_4) for a variety of conditions.¹ The energies considered in that study extend to levels well above threshold. The results clearly show that the spectral mode identities are retained on the time scale (10 ps) used in the study at quite high energies. That is, even at energies well above the reaction threshold polyatomic molecules behave quasiperiodically. There is significant mode mixing, but it is not global – the IVR occurs, on this time scale, among subsets of the molecular modes. In this project, we extended this work by

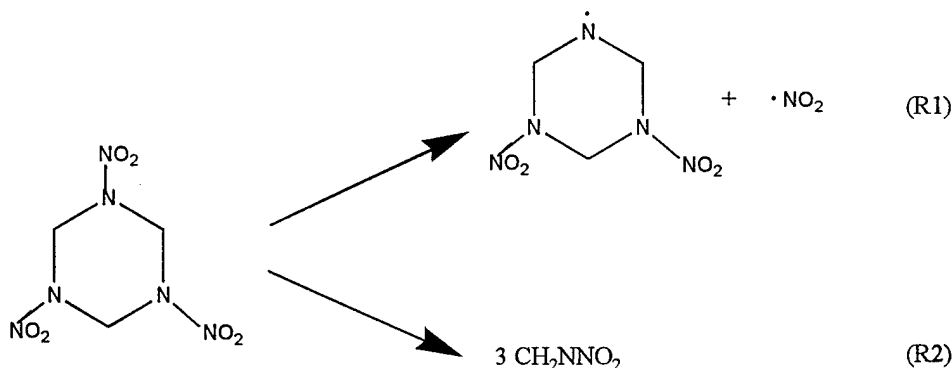
computing power spectra for RDX for various initial conditions.² We were particularly interested in determining the nature of the dynamics at levels of excitation corresponding to those in infrared multiphoton dissociation (IRMPD) experiments. The computed power spectra consist of well-defined bands for the distinct internal coordinates. The bands for individual coordinates are readily distinguishable in the power spectra although they are significantly broadened. Nevertheless, there is considerable mode mixing. That is, although the molecular vibrations retain their identities, they rapidly exchange energy. In fact, we found that this is true of the classical motions even at the zero-point energy level, and that the spectra for excitation energies corresponding to those in IRMPD experiments are not much different from those at the zero-point energy level. Furthermore, the spectral broadening in RDX is much greater than that observed for the smaller molecules in our first study.¹

The observed enhanced line broadening in RDX may be due to the fact that it undergoes chair-to-boat conformational changes. Eigen,³ in 1964, suggested that very fast reactions might affect vibrational spectra. If this is true, then the rates of reactions might be determined from vibrational line shapes, as is done from NMR spectra. There is, of course, and this is the main problem, a significant difference in the time scales for NMR and vibrations. We carried out a series of calculations to determine the influence of crossings of a transition state (*i.e.*, reactions) on mode mixing (power spectral line broadening and shifting). These studies were done for intramolecular isomerizations in HONO, methyl nitrite, and RDX.^{4,5} We found that mode mixing is indeed enhanced by repeated crossings of a barrier. We attempted to calculate rates of reactions from the line widths, however, we were unable to obtain quantitatively accurate results although there was qualitative agreement with the rates obtained from the first-order decay curves. We found that different types of normal modes are affected differently by the crossings of the barrier; the extent of broadening depends on the nature of the mode. Thus, this causes ambiguity in the determination of the reaction rates from spectral line broadening.

The molecule of prime interest in our program is RDX, and one of the goals in this work is to develop an accurate potential energy surface (PES) for the unimolecular dissociation of RDX. We developed a new PES for RDX dissociation based on

spectroscopic and thermodynamics data, some *ab initio* results from the literature, and assumed behavior for the forces between critical points on the surface.⁷ This PES represents a refinement of our earlier one;⁸ it is based similar functional forms and the values of the parameters were determined in a similar fashion.

The PES describes the unimolecular dissociation of RDX in the gas phase. We have assumed, based on the IRMPD results of Zhao, Hints, and Lee,⁹ that the primary decomposition reactions of RDX are triple bond-fission that breaks the ring into three methylene nitramine (CH_2NNO_2) molecules and simple N-N bond rupture to eliminate NO_2 :



Since there is some uncertainty (and lack of agreement) about the energy barrier to ring fission, we performed classical trajectory calculations on three PESs that are similar except for the barrier height for that reaction channel. The barrier height to the simple bond rupture is generally accepted to be in the range 45-50 kcal/mol; we used 48 kcal/mol in our models. We calculated unimolecular dissociate rates for PESs with barrier to the ring fission of 37, 56, and 71 kcal/mol. The value of 71 kcal/mol was considered because it is a prediction based on some *ab initio* studies. Only the PESs with the 37 kcal/mol barrier to ring fission gives results in accord with the Zhao *et al.*⁹ experiments. They reported the ratio of the rate of ring fission to that of the simple bond rupture to be about two. Our results are for an approximate PES and thus cannot be used to definitely determine the kinetic parameters (*e.g.*, barrier heights), however, our studies strongly indicate that the barrier to ring fission must be lower than that for simple N-N bond rupture in order to match the experimental result.

Training Scientists

One of the goals of this project was to train Ph.D. students in a research areas of interest to DoD. The grant provided the principal support for Candee C. Chambers, and support for one year for Gary Thacker. Dr. Chambers completed the Ph.D. degree in 1994. She spent two years as Postdoctoral Research Associate at the University of Minnesota working on another DoD-supported research project. She is currently an Assistant Professor of Chemistry at Mercyhurst College, Erie, PA.

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Candee C. Chambers, Ph.D., July, 1994. Title: *Dynamics of Polyatomic Molecules. I. Enhancement of Vibrational Mode Mixing due to Intramolecular Conversions. II. Chemical Reactions in Cyclic Nitramines.*

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